2384

ACTION OF PERSPIRATION ON LEATHER*

Part III: A LABORATORY TEST FOR THE ASSESSMENT OF THE RELATIVE STABILITY OF LEATHERS TO PERSPIRATION

J. H. Bowes and C. W. Cater

Summary

The factors to be considered in the selection of a test for the assessment of the resistance of leathers to perspiration are discussed. Any such test must involve treatment with a synthetic perspiration coupled with a period of exposure to moist heat. Mechanical action is an important factor in wear but it is difficult to incorporate satisfactorily into a test.

The synthetic perspiration used should contain the same constituents as natural perspiration in the same relative proportions and should have the same buffering capacity. The temperature of exposure to moist heat should not exceed 40°C. A test based on successive extraction with a synthetic perspiration corresponding in composition to a fourfold concentration of natural perspiration at 40°C is suggested. Damage resulting at each stage can be assessed objectively or by relevant physical tests. The degree to which the shrinkage temperature is maintained is an indication of potential resistance to more prolonged exposure to moist heat.

The deterioration of leather in wear is frequently ascribed to perspiration and various tests have been devised for testing the resistance of leather to such deterioration, none of which has been entirely satisfactory.

Two of the main factors involved in the deterioration of leather by perspiration are the moist heat associated with the production of the perspiration and the effect of the constituents of perspiration in mitigating or accelerating the damage resulting from this. Mechanical action also plays a part in accelerating deterioration and Roddy and Lollar[1] considered this feature so important that the test suggested by them for shoe upper leather incorporated a flexing action. The stresses applied to leather are various, however, involving not only flexing but pressure, abrasion, etc., and it is difficult to incorporate such effects into a general test for resistance to perspiration and even if this could be done it is doubtful whether the results would justify the complicated procedures involved. Efforts were, therefore, directed towards the development of a simple static test. The present paper surveys some of the factors which should be considered in designing such a test. A method involving successive extraction of the leather with a synthetic perspiration at 40°C is suggested as the best compromise.

Composition of Perspiration and Amount to be Applied

The composition of human perspiration as reported by Kuno[2] is given in Table I. The pH values recorded for persiration usually lie between 6 and 7, rising to 8·0 or 8·5 on standing[2].

* The work reported in this paper forms part of Research Programme sponsored by the U.S. Department of Agriculture under the authority of U.S. Public Law 480.

TABLE 1

Composition of Perspiration according to Kuno[2]

	g per 100 g
Sodium chloride	0·3 - 0·5
Lactic acid	0·1 - 0·3
Total-nitrogen	0·02 - 0·05
Ammonia-nitrogen	0·003 - 0·01
Amino acids	0·05
Urea	0·05

It is clear from recent work[3,4] that damage to chrome leather is primarily due to the lactate ions present in the perspiration which, by competition for the chromium, cause detannage. The extent to which this occurs appears to be directly proportional to the amount of lactate to which the leather is exposed[3].

The rise in pH due to the absorption of perspiration will also be a factor contributing to the detannage of chrome leather and with vegetable tanned leathers is probably the the primary cause of damage[5,6]. With vegetable-chrome combination tanned leathers displacement of chromium from the protein by lactate is to some extent mitigated by the presence of vegetable tan[7] and the increase in pH is reduced by the acid released from the chromium complex by vegetable tan.

Various synthetic perspiration have been suggested some of which differ appreciably from the figures given by Kuno[2]. There would seem to be little justification for this and in particular for the use of high concentrations of urea. This compound will in any case be rapidly converted to ammonia by bacterial action and its importance is related to the increased alkalinity derived from it rather than to any specific effect.

It is obviously important that the pH and buffering capacity of the synthetic perspiration should be as nearly as possible the same as that of natural perspiration and also that it should be readily reproduced. Rather than rely on the conversion of urea to ammonia under the relatively aseptic conditions of the test it is probably better to add the required amount of a suitable weak alkali. Titration of a 100 ml of natural perspiration from pH 8·5, its initial value, to pH 5·0 the point at which titration of sodium lactate becomes predominant, required 4 to 5 ml of 0·1N acid. This buffering action is presumably related to the phosphate and bicarbonate content of the sweat and it is suggested that either of these should be added in the appropriate amounts to the perspiration mixture used.

In the absence of any argument to the contrary the relative proportions of the other constituents should be based on the values given by Kuno[2], namely, sodium lactate, sodium chloride and amino acids in the ratio 1:1:0·1. The upper limit for sodium lactate has been preferred as being more realistic in view of the high figures for foot perspiration recently reported by Pettit[8]. Any detanning effect of amino acids will be related to their α-carboxyl and amino groups, and there appears to be no reason to prefer any particular amino acid rather than another. Glycine, the simplest and cheapest amino acid, may as well be used.

Figures quoted for the volume of perspiration secreted per sq. cm. of body surface per hour vary from 0·02 to 0·1 ml depending on the conditions[9]. Over the hands and feet, the areas most likely to come into contact with leather the amounts may well be considerably greater. Thus, it is very difficult to estimate the amount of perspiration a leather is likely to absorb in wear, especially in the case of upper leather where a sock is generally interposed.

However, on the basis of the above figures it would probably not be unreasonable to assume that a thin gloving leather having a surface area of about 50 sq. cm. per g. might absorb as much as 20 ml of perspiration (≡ about 0·05 g. sodium lactate) per gram leather per hour during profuse sweating, whereas a thicker insole leather, surface area of the order 8 sq. cm. per g. will only absorb about one-sixth of this amount. Such calculations give some indications of the amounts of perspiration which should be used in any test.

Method of Application and Test Conditions

Ideally to simulate as far as possible the conditions in wear the perspiration should be applied gradually as a dilute solution to the underside of the leather with intermittent exposure to moist heat and drying out. This is a tedious procedure and experience has shown that it is difficult to apply a given amount evenly to the leather.

Methods involving the immersion of the leather in a solution of perspiration are less realistic but were found to give more reproducible results[3].

The necessity of including some period of exposure to moist heat in any test so that the effect of the chemical consituents of the perspiration on the stability of the leather has time to become evident has been clearly demonstrated by earlier work[3,4]. The question is how severe should this exposure be and to what extent is it permissible to accelerate the test by the use of raised temperatures. Tests have shown that the relative resistance of vegetable, chrome, semichrome and chrome retan leathers to moist heat is not the same at 60° as at 40° and since the highest temperature likely to be met with in wear is about 35° it is probably not justifiable to use temperatures above 40°c.

With chrome leathers it has been found that the degree of damage resulting from exposure to moist heat is closely related to the shrinkage temperature[3,4]. The extent to which the shrinkage temperature is reduced by treatment in perspiration would, therefore, appear to offer some indication of the potential stability of the leather.

Re-examination of earlier results show that with this type of leather the shrinkage temperature falls directly with the logarithm of the amount of lactate applied (Fig. 1). If the leather is extracted with, say, three concentrations of synthetic perspiration—or perhaps better still—three or more successive times with one concentration, it should be possible to determine the amount required to reduce the shrinkage temperature below some predetermined danger level, say, 65° or 70°c and this should serve as a criterion of the relative resistance to be expected in more prolonged exposure to moist heat.

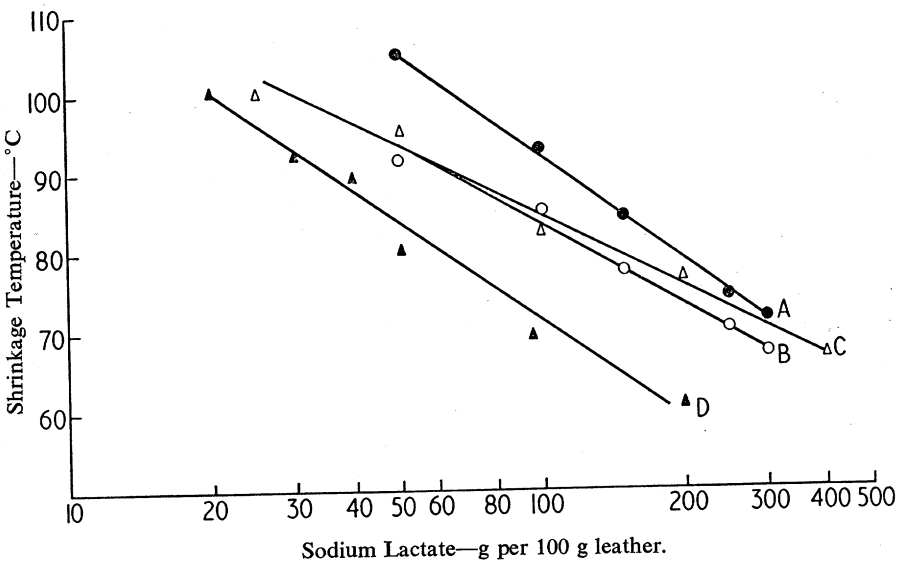

FIGURE 1

Extraction of four leathers with Various Concentrations of Sodium Lactate.

● ——— ● Leather A—successive extraction with 2% sodium lactate at 40°, each with 25 ml per gram leather for four days.

○ ——— ○ Leather B—successive extraction with 2% sodium lactate at 40°, each with 25 ml per gram leather for four days.

△ ——— △ Leather C—single extraction at 40° for four days with different concentrations.

▲ ——— ▲ Leather D—single extraction at 40° for four days with different concentrations.

Selected Method of Test

Bearing in mind the various considerations discussed above the following procedure for the comparison of the relative stability of different leathers to perspiration is suggested.

It is recommended that the leather be extracted several times with the following solution, using 20 ml per g leather, each extraction being for four or five days at 40°c.

2% Sodium Lactate
2% Sodium Chloride
0·2% Glycine
0·34% Sodium Bicarbonate ≡ 20 ml 0·1M per 100 ml.

Several pieces of leather should be included and one removed for test after each extraction, the volume of solution for the next extraction being adjusted accordingly.

In this test the composition of the artificial perspiration has been selected to correspond as nearly as possible to that of natural perspiration and the amounts applied to cover a range which might be expected in wear.

The above solution is approximately four times the concentration of natural perspiration so that each of the extractions is equivalent to the absorption of about 80 ml perspiration per gram of leather. No allowance is made for the fact that in wear perspiration is absorbed by one side of the leather only and hence that a thin leather will absorb more per gram than a thicker one. With the above amounts each extraction is the equivalent of about four hours' exposure to profuse sweating with a thin leather and about 24 hours with a thicker leather such as insole. It could be argued, therefore, that the amounts used should be calculated on an area basis and this may be desirable, particularly when leathers of varying thickness are to be compared.

After drying out the leathers are assessed for feel and appearance and the number of extractions which they can withstand before there is appreciable damage serves as a useful measure of resistance. If desired, physical tests relevant to the type of leather can be made and stability related either to the number of extractions the leather will withstand before showing some given degree of damage, or to the degree of damage resulting from a given number of extractions. The level to which the shrinkage temperature is reduced gives an indication of the potential stability of the leathers to further exposure to moist heat. Such a test is most useful in comparing chrome leathers with which the shrinkage temperature decreases progressively with the amount of perspiration applied, and an estimate of their relative stabilities can be made by plotting the shrinkage temperature against the number of extractions and recording the number necessary to reduce the shrinkage temperature to some predetermined danger level, say, 70°C. With aldehyde, chrome-aldehyde or -syntan combination tanned leathers the level to which the shrinkage temperature is reduced serves as a guide to potential stability, for after falling rapidly at first as the chromium is extracted, it will, if the additional tanning agent imparts stability, remain at a constant level corresponding to tannage with that material. The test is less applicable to leathers containing vegetable tannins since changes in the tans rather than detannage is there concerned. However, the appearance of the leathers after each extraction should be a useful guide to resistance.

Various leathers have been tested by the proposed procedure and the results are reported in Table II.

With the chrome leathers damage became apparent when the shrinkage temperature was reduced to about 65°C. With glutaraldehyde tanned leathers the shrinkage temperature never falls below about 74°C and there is little damage to the leather. The good resistance of these leathers to perspiration has also been confirmed in many other tests. The same is also true of the glutaraldehyde-chrome combination tanned leathers, more particularly when the glutaraldehyde tannage is carried out first.

Although the present test enables a useful prognosis to be made of the relative resistance of leathers to perspiration, it does not necessarily predict

TABLE II

Successive Extraction of Leathers with a Synthetic Perspiration

	Number of Extractions						
	0	1	2	3	4	5	6
	Shrinkage Temperature °C						
Full Chrome Leathers							
Upper—3·2% Cr_2O_3	106	99	86	77	*	73 *	72 *
Upper—3·1% Cr_2O_3	100	93	81	77	75 *	71 *	**
Clothing—5·4% Cr_2O_3	117			92	84 *	71 *	68 **
—4·1% Cr_2O_3	112		60 **	***	53 ***	****	51 *****
Gloving—1·8% Cr_2O_3	90	65 *	60 **	***	****	*****	*****
—2·1% Cr_2O_3	100	72	64 *	63 **	***	****	*****
—2·7% Cr_2O_3	102	75	70 *	67 **	65 **	***	****
—3·6% Cr_2O_3	108	82	75	72 *	69 *	63 **	55 ***
Glutaraldehyde Tanned Leathers							
Clothing	81		74		74 *	*	74 *
Gloving	76			76		*	74 *
	83		78		78	*	78 *
	80		77		77		76 *
Chrome-Glutaraldehyde Tanned Leathers							
Clothing Leather retanned glutaraldehyde 3·5% Cr_2O_3	99		86	*	75 *	**	74 ***
Gloving Leather pretanned glutaraldehyde —2·7% Cr_2O_3	92	82	—	77	— *	76 *	*
Vegetable-Tanned Leather							
Vegetable tanned split hide	77		*	*	**	88 **	***
Vegetable-Chrome Split-hide—1·2% Cr_2O_3	96	89	*	85 *	*	85 *	83 **

* First obvious signs of damage
***** Very damaged

their resistance to deterioration in wear when many other factors are involved, and in particular the suitability of the leather for the types of mechanical stresses it must undergo.

British Leather Manufacturers' Research Association,
Milton Park,
Egham, Surrey.

References

1. Roddy, W. T. and Lollar, R. M., *J. Amer. Leath. Chem. Ass.*, 1955, **50,** 180.
2. Kuno, Y., "Human Perspiration", Thomas, Springfield, 1956, p. 223.
3. Bowes, J. H. and Moss, J. A., *J. Soc. Leath. Tr. Chem.*, 1960, **44,** 419.
4. Bowes, J. H. and Raistrick, A. S., *J. Amer. Leath. Chem. Ass.*, 1963, **58,** 190.
5. Grassman, W. and Stadler, P., *Leder,* 1953, **4,** 219.
6. Grassman, W. and Stadler, P., *Leder,* 1956, **7,** 8.
7. Bowes, J. H. and Moss, J. A., *J. Amer. Leath. Chem. Ass.*, 1962, **57,** 625.
8. Pettit, D., *J Soc Leath. Tr. Chem.*, 1961, **45,** 415.
9. Kuno, Y., Human Perspiration, Thomas, Springfield, 1956, p. 251.
10. Raistrick, A. S., *J. Amer. Leath. Chem. Ass.*, 1961, **56,** 616.

In this test the composition of the artificial perspiration has been selected to correspond as nearly as possible to that of natural perspiration and the amounts applied to cover a range which might be expected in wear.

The above solution is approximately four times the concentration of natural perspiration so that each of the extractions is equivalent to the absorption of about 80 ml perspiration per gram of leather. No allowance is made for the fact that in wear perspiration is absorbed by one side of the leather only and hence that a thin leather will absorb more per gram than a thicker one. With the above amounts each extraction is the equivalent of about four hours' exposure to profuse sweating with a thin leather and about 24 hours with a thicker leather such as insole. It could be argued, therefore, that the amounts used should be calculated on an area basis and this may be desirable, particularly when leathers of varying thickness are to be compared.

After drying out the leathers are assessed for feel and appearance and the number of extractions which they can withstand before there is appreciable damage serves as a useful measure of resistance. If desired, physical tests relevant to the type of leather can be made and stability related either to the number of extractions the leather will withstand before showing some given degree of damage, or to the degree of damage resulting from a given number of extractions. The level to which the shrinkage temperature is reduced gives an indication of the potential stability of the leathers to further exposure to moist heat. Such a test is most useful in comparing chrome leathers with which the shrinkage temperature decreases progressively with the amount of perspiration applied, and an estimate of their relative stabilities can be made by plotting the shrinkage temperature against the number of extractions and recording the number necessary to reduce the shrinkage temperature to some predetermined danger level, say, 70°C. With aldehyde, chrome-aldehyde or -syntan combination tanned leathers the level to which the shrinkage temperature is reduced serves as a guide to potential stability, for after falling rapidly at first as the chromium is extracted, it will, if the additional tanning agent imparts stability, remain at a constant level corresponding to tannage with that material. The test is less applicable to leathers containing vegetable tannins since changes in the tans rather than detannage is there concerned. However, the appearance of the leathers after each extraction should be a useful guide to resistance.

Various leathers have been tested by the proposed procedure and the results are reported in Table II.

With the chrome leathers damage became apparent when the shrinkage temperature was reduced to about 65°C. With glutaraldehyde tanned leathers the shrinkage temperature never falls below about 74°C and there is little damage to the leather. The good resistance of these leathers to perspiration has also been confirmed in many other tests. The same is also true of the glutaraldehyde-chrome combination tanned leathers, more particularly when the glutaraldehyde tannage is carried out first.

Although the present test enables a useful prognosis to be made of the relative resistance of leathers to perspiration, it does not necessarily predict

TABLE II

Successive Extraction of Leathers with a Synthetic Perspiration

	Number of Extractions						
	0	1	2	3	4	5	6
	Shrinkage Temperature °C						
Full Chrome Leathers							
Upper—3·2% Cr_2O_3	106	99	86	77	*	73 *	72 *
Upper—3·1% Cr_2O_3	100	93	81	77	75 *	71 *	**
Clothing—5·4% Cr_2O_3	117			92	84 *	71 *	68 **
—4·1% Cr_2O_3	112		60 **	***	53 ***	****	51 *****
Gloving—1·8% Cr_2O_3	90	65 *	60 **	***	****	*****	*****
—2·1% Cr_2O_3	100	72	64 *	63 **	***	****	*****
—2·7% Cr_2O_3	102	75	70 *	67 **	65 **	***	****
—3·6% Cr_2O_3	108	82	75	72 *	69 *	63 **	55 ***
Glutaraldehyde Tanned Leathers							
Clothing	81		74		74 *	*	74 *
Gloving	76			76		*	74 *
	83		78		78	*	78 *
	80		77		77		76 *
Chrome-Glutaraldehyde Tanned Leathers							
Clothing Leather retanned glutaraldehyde 3·5% Cr_2O_3	99		86	*	75 *	**	74 ***
Gloving Leather pretanned glutaraldehyde —2·7% Cr_2O_3	92	82	—	77	— *	76 *	*
Vegetable-Tanned Leather							
Vegetable tanned split hide	77		*	*	**	88 **	***
Vegetable-Chrome Split-hide—1·2% Cr_2O_3	96	89	*	85 *	*	85 *	83 **

* First obvious signs of damage
***** Very damaged

their resistance to deterioration in wear when many other factors are involved, and in particular the suitability of the leather for the types of mechanical stresses it must undergo.

British Leather Manufacturers' Research Association,
Milton Park,
Egham, Surrey

References

1. Roddy, W. T. and Lollar, R. M., *J. Amer. Leath. Chem. Ass.*, 1955, **50,** 180.
2. Kuno, Y., "Human Perspiration", Thomas, Springfield, 1956, p. 223.
3. Bowes, J. H. and Moss, J. A., *J. Soc. Leath. Tr. Chem.*, 1960, **44,** 419.
4. Bowes, J. H. and Raistrick, A. S., *J. Amer. Leath. Chem. Ass.*, 1963, **58,** 190.
5. Grassman, W. and Stadler, P., *Leder,* 1953, **4,** 219.
6. Grassman, W. and Stadler, P., *Leder,* 1956, **7,** 8.
7. Bowes, J. H. and Moss, J. A., *J. Amer. Leath. Chem. Ass.*, 1962, **57,** 625.
8. Pettit, D., *J Soc Leath. Tr. Chem.*, 1961, **45,** 415.
9. Kuno, Y., Human Perspiration, Thomas, Springfield, 1956, p. 251.
10. Raistrick, A. S., *J. Amer. Leath. Chem. Ass.*, 1961, **56,** 616.